Performance evaluation of a sorbent tube sampling method using short path thermal desorption for volatile organic compounds

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Air sampling, using sorbents, thermal desorption and gas chromatography, is a versatile method for identifying and quantifying trace levels of volatile organic compounds (VOCs). Thermal desorption can provide high sensitivity, appropriate choices of sorbents and method parameters can accommodate a wide range of compounds and high humidity, and automated short-path systems can minimize artifacts, losses and carry-over effects. This study evaluates the performance of a short-path thermal desorption method for 77 VOCs using laboratory and field tests and a dual sorbent system (Tenax GR, Carbosieve SIII). Laboratory tests showed that the method requirements for ambient air sampling were easily achieved for most compounds, *e.g.*, using the average and standard deviation across target compounds, blank emissions were $\leqslant 0.3$ ng per sorbent tube for all target compounds except benzene, toluene and phenol; the method detection limit was 0.05 ± 0.08 ppb, reproducibility was $12 \pm 6\%$, linearity, as the relative standard deviation of relative response factors, was $16 \pm 9\%$, desorption efficiency was $99 \pm 28\%$, samples stored for 1–6 weeks had recoveries of $87 \pm 9\%$, and high humidity samples had recoveries of $102 \pm 12\%$. Due to sorbent, column and detector characteristics, performance was somewhat poorer for phenol groups, ketones, and nitrogen containing compounds. The laboratory results were confirmed in an analysis of replicate samples collected in two field studies that sampled ambient air along roadways and indoor air in a large office building. Replicates collected under field conditions demonstrated good agreement except for very low concentrations or large (>4 l volume) samples of high humidity air. Overall, the method provides excellent performance and satisfactory throughput for many applications.

Introduction

Air sampling using adsorbents followed by thermal desorption and chromatographic analysis can provide excellent performance for many volatile organic compounds (VOCs) and broad applicability to ambient, workplace, and indoor environments.[1–4] This method offers a number of advantages in comparison to competing methods. For example, thermal desorption of sorbents offers higher sensitivity than chemical methods since the sample is not diluted.[5] Sorbent tube sampling can achieve high recovery of polar and reactive compounds, which can pose problems for whole air samples collected in canisters.[6] Sorbent tubes themselves are easy to condition and small in size, facilitating collection, transport and storage. The associated sampling systems are also small and relatively inexpensive. Several thermal desorber systems are available that automate tasks of desorption, concentration (focusing) of analytes onto cryogenic traps or cooled sorbents, and injection into a gas chromatograph (GC). Of course, any sampling method involves compromises, but many if not most sampling and analysis issues for sorbent tubes have been worked out in a satisfactory manner. For example, problems of breakthrough in sampling and artifact formation in analysis can be minimized by appropriate sorbent selection and use. Water and water vapor, which can interfere with collection and analysis, can be managed using hydrophobic sorbents, dry purges,[3,7] and other techniques. Finally, problems such as sample degradation due to contact with the heated transfer line from the desorber to the GC inlet,[8] and carry-over from previous samples can be avoided or minimized using short-path desorber systems, which have recently become available.

The performance of a sorbent sampling/thermal desorption method depends on many factors, including the target compounds (*e.g.*, concentration, species and mixture), the method (*e.g.*, sorbent selection, procedures for conditioning, desorption, separation and analysis of VOCs), and environmental conditions present during sampling (*e.g.*, temperature and humidity). Performance evaluations are time consuming and expensive, are often application- and method-specific, and there are genuine issues concerning the relevance of laboratory evaluations to the performance expected in the field. In consequence, the literature contains relatively few performance evaluations. In practice, most users attempt to collect replicates for 10 or 20% of the samples, and agreement among replicates suggests that performance is acceptable. While replicates are needed for quality assurance purposes, more comprehensive investigations are needed in order to assess the performance of an air sampling system in a robust and generalizable manner.

This study provides a comprehensive performance evaluation of a sorbent sampling and analysis method using a short-path thermal desorption system with the aim of providing a realistic description of system performance. The study includes laboratory, ambient and indoor applications using 77 VOCs as test compounds. The laboratory studies allow separation of the factors that affect method performance. Analysis of duplicate samples in two field studies demonstrated the performance of the method under real-life conditions. The evaluation includes an assessment of blank emissions, artifact formation, method detection limit, reproducibility, linearity, desorption efficiency, storage stability, and water management effectiveness. Optimal desorption and analysis conditions are suggested.

Methods and materials

Sorbent tube preparation and conditioning

This study used 10 cm long, 6 mm od, 4 mm id stainless-steel sorbent tubes with tapered screw threads on both ends
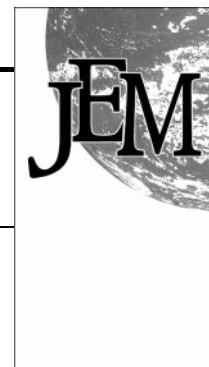
Table 1 Chemical properties for target compounds, including chemical abstract number (CAS); molecular weight (M_w); boiling point (BP); melting point (MP), target ion and qualifier ions[a]

Compound	CAS No.	M_w/u	BP/°C	MP[b]/°C	Target ion/u	Qualifier ion/u
1,2-Dichloroethylene (*trans, E*)	156-60-5	96.9	48	−50	61	96
tert-Butyl methyl ether	1634-04-4	86.0	55	NA	73	57
1,1-Dichloroethane	75-34-3	99.0	57	−97	63	83
Propanenitrile	107-12-0	55.1	97	−93	54	55
Hexane	110-54-3	86.2	69	NA	57	86
Methacrylonitrile	126-98-7	67.1	90	−36	41	67
1,2-Dichloroethylene (*cis, Z*)	156-59-2	96.9	60	−81	61	96
2-Butanone	78-93-3	72.0	80	NA	43	72,57
2,2-Dichloropropane	594-20-7	113.0	69	−34	77	97, 41
Bromochloromethane	74-97-5	129.4	68	−87	49	130
Chloroform	67-66-3	119.0	61	−64	83	47
Methyl acrylate	96-33-3	86.1	81	<−75	55	85, 27
Tetrahydrofuran	109-99-9	72.1	67	−109	42	72
1,1,1-Trichloroethane	71-55-6	133.4	74	−30	97	61, 117
1,2-Dichloroethane	107-06-2	99.0	84	−35	62	49, 98
Butyl chloride	109-69-3	92.6	78	−123	56	41, 27
1,1-Dichloropropane	563-58-6	111.0	77	NA	75	110
Benzene	71-43-2	78.0	80	6	78	50
Carbon tetrachloride	56-23-5	153.8	77	−23	117	82
Chloroacetonitrile	107-14-2	75.5	124	NA	75	48
1,2-Dichloropropane	78-87-5	113.0	97	−100	63	76, 41
Trichloroethylene	79-01-6	131.4	87	−73	130	95
Dibromomethane	74-95-3	173.9	97	−53	174	93
2-Nitropropane	79-46-9	89.0	120	NA	43	41, 27
Bromodichloromethane	75-27-4	163.8	90	−57	83	129
Methyl methacrylate	80-62-6	100.1	101	NA	41	69, 100
1,1-Dichloro-2-propanone	513-88-2	127.0	120	NA	43	83
1,3-Dichloropropene (*cis, Z*)	10061-01-5	111.0	112	NA	75	110
Isobutyl methyl ketone	108-10-1	100.2	117	−85	43	58, 85, 100
Toluene	108-88-3	92.0	111	−95	91	92
1,3-Dichloropropene (*trans, E*)	10061-02-6	111.0	112	NA	75	110, 49
1,1,2-Trichloroethane	79-00-5	133.4	114	−37	97	83, 61
1,3-Dichloropropane	142-28-9	113.0	120	−100	76	41
Dibromochloromethane	124-48-1	208.3	120	NA	129	127
Ethyl methacrylate	97-63-2	114.2	117	NA	69	41, 99, 114
2-Hexanone	591-78-6	100.2	128	−57	43	58, 71
1,2-Dibromoethane	106-93-4	187.9	132	98	107	109, 27
Tetrachloroethene	127-18-4	165.8	121	−19	166	129
Chlorobenzene	108-90-7	112.6	132	−46	112	77
1,1,1,2-Tetrachloroethane	630-20-6	167.9	131	−70	131	117, 95
Ethylbenzene	100-41-4	106.0	136	−95	91	106
p-Xylene	106-42-3	106.2	138	13	91	106
m-Xylene	108-38-3	106.2	139	−48	91	106
Bromoform	75-25-2	252.8	149	NA	173	252
Styrene	100-42-5	104.0	145	NA	104	78
o-Xylene	95-47-6	106.2	144	−25	91	106
1,1,2,2-Tetrachloroethane	79-34-5	167.9	146	−36	83	131, 168
1,2,3-Trichloropropane	96-18-4	147.4	124	NA	75	110
Isopropylbenzene (cumene)	98-82-8	120.0	153	NA	105	120
Bromobenzene	108-86-1	157.0	156	−30	77	156
1,4-Dichlor-2-butene (*trans, E*)	110-57-6	125.0	156	1–3	75	89, 124
a-Pinene (1*R*)-(+)	7785-70-8	136.2	155	−55	93	77, 105
2-Chlorotoluene	95-49-8	126.6	159	−35	91	126
n-Propylbenzene	103-65-1	120.2	159	−100	91	120
4-Chlorotoluene	106-43-4	126.6	162	8	91	126
1,3,5-Trimethylbenzene	108-67-8	120.2	165	−45	105	120
Pentachloroethane	76-01-7	202.3	162	−29	167	117
Phenol	108-95-2	94.1	182	40–42	94	66
tert-Butylbenzene	98-06-6	134.2	169	−58	119	91, 134
1,2,4-Trimethylbenzene	95-63-6	120.2	170	−44	105	120
1,4-Dichlorobenzene	106-46-7	94.5	189	53	146	111, 75
1,3-Bichlorobenzene	541-73-1	147.0	173	−25	146	111, 75
sec-Butylbenzene	135-98-8	134.2	173	−75	105	134
p-Isopropyltoluene	99-87-6	136.2	177	−68	119	134
Limonene (*R*)-(+)	5989-27-5	136.2	177	−97	68	93, 136
1,2-Dichlorobenzene	95-50-1	147.0	181	−17	146	111, 75
n-Butylbenzene	104-51-8	134.2	183	−88	91	134
o-Cresol	95-48-7	108.1	191	32–34	108	79, 90
Hexachloroethane	67-72-1	236.7	Sublimes	190–195	166	201, 117
p-Cresol	106-44-5	108.1	202	35	107	77
m-Cresol	108-39-4	108.1	202	12	107	77
1,2-Dibromo-3-chloropropane	96-12-8	236.3	196	NA	157	75
Nitrobenzene	98-95-3	123.0	211	17	123	77, 51
1,2,4-Trichlorobenzene	120-82-1	181.5	213	17	180	145, 109
Naphthalene	91-20-3	228.3	Sublimes	357	128	102
1,2,3-Trichlorobenzene	87-61-6	181.5	219	53–54	180	145
Hexachlorobutadiene	87-68-3	260.8	215	−19	225	260, 190

[a] Target ion is used for quantification. Ions in bold used for identification. CAS, M_w, BP and MP from ref. 8. [b] NA means not available.

(Scientific Instrument Services, Inc., Ringoes, NJ, USA). Following recommendations for ambient air sampling applications,[3] each tube was packed at the upstream (sampling) end with 3 mm silanized glass wool, 160 mg 60/80 mesh Tenax GR (Supelco, Bellefonte, PA, USA) (polyester–phenyl ether with 23% graphitized carbon), then 3 mm silanized glass wool, followed by 70 mg Carbosieve SIII (Supelco, Inc. Bellefonte, PA, USA; 60/80 mesh), and finally 3 mm silanized glass wool at the downstream end. The sorbent bed was positioned at least 15 mm from the tube end. Packed tubes were conditioned at 325 °C in a 24 tube conditioning oven (Model A-24, Scientific Instrument Services) for 6 h with a 25–50 ml min^{-1} reverse flow (opposite to sampling direction) of high purity (99.999%) helium. After conditioning, stainless-steel caps with Teflon$^®$ seals were screwed onto both ends of the tube. The tubes were then wrapped in previously baked aluminium foil and stored in a glass jar at 4 °C. Including blanks, calibration tubes and quality control samples, the laboratory component of this study used 30 tubes, the ambient study used 20 tubes, and the indoor air study used 10 tubes.

VOC standards

Selected on the basis of their occurrence and health effects, the 77 VOCs tested included a number of aliphatic, aromatic, and halogenated compounds, as well as several ketones and phenols (Table 1). The selected VOCs have boiling points from 47 to 219 °C, and molecular weights from 72 to 261 u.[9] Many compounds on the US EPA TO-14[10] and TO-15[11] lists of ambient air toxics were included. Several of the listed compounds (*e.g.*, buta-1,3-diene and acetaldehyde) were not included due to their low boiling point and high reactivity. High capacity or treated adsorbents (such as DNPH-coated silica gel) are needed to collect these compounds.

Three commercially prepared VOC standards (EPA 524 VOC Mix, EPA 524 Rev. 4 Update Mix, EPA 524.2 Ketone Mix; Supelco Inc., Bellefonte, PA, USA) were further diluted in methanol (99.9%, Fisher Scientific, Inc., NJ, USA) to form a 400 µg ml^{-1} (individual compound) stock solution. This solution was further diluted in pentane (99.9%, Aldrich Chemical, Co., WI, USA) to obtain five VOC standards ranging from 0.2 to 20 ng µl^{-1}. Additionally, phenol and terpene standards were prepared using neat chemicals to obtain solutions at similar concentrations. All standards were prepared on the day of use, and stored at 4 °C.

Laboratory performance evaluation

Blank emissions. Blank emissions and artifact formation, which can affect method sensitivity and overall performance, were determined using a total of 17 freshly cleaned tubes. To evaluate any emissions that might result from storage, 3 cleaned tubes were analyzed after being stored at 4 °C for 1 week, and 3 others after 6 weeks. These and all other laboratory tests were performed at 23 °C.

To investigate influences of humidity on the performance of sorbent tube sampling, 5 tubes were exposed to 4 l of 49% relative humidity (RH) air, and 4 others to 4 l of 88% RH air; these tubes were analyzed immediately after exposure. VOC-free water was prepared by first sparging distilled water with ultrapure (99.999%) nitrogen for 6 h. A 180 or 330 µl aliquot (for 49 and 88% RH, respectively) of VOC-free water was injected into an evacuated and clean 6 l Summa stainless-steel canister, which was then pressurized to 30 psi using clean dry air generated using an air purification system (AADCO model 737, Clearwater, FL, USA) and a liquid nitrogen trap. A total of 4 l of humidified "zero" air from the canister was passed through the sorbent tube at 100–150 ml min^{-1}, controlled by a rotameter. Nominal sampling volumes are 3 l (see below), thus, the humidified experiments were performed under somewhat adverse conditions. In all, tubes were exposed to 40 µl of water vapor in the 49% RH experiment, and 72 µl in the 88% RH experiment.

Method detection limit. Following US EPA guidance,[3] the method detection limit (MDL) for each VOC was determined by making 7 replicate measurements of a concentration near the expected detection limit (within a factor of 5). The MDL was calculated as the standard deviation of the replicate determinations multiplied by 3.14, the 99% confidence interval for $n = 7$ (from Student's t distribution).

Reproducibility. Reproducibility was determined by spiking sorbent tubes in triplicate or quadruplicate with 2 µl of standards using a stainless-steel "T" type loader (Scientific Instrument Services), a helium flow rate of ~40 ml min^{-1} through the T, and a 10 µl liquid syringe (Hamilton, Reno, NV, USA). In this step, each tube was loaded with 0.4–40 ng per VOC. Assuming a 3 l air sample, these loadings are equivalent to air concentrations of from 0.13 to 13.3 µg m^{-3}. Reproducibilities were expressed as the relative standard deviation (RSD) for each concentration.

Linearity. The linearity of the 5-point calibration was calculated as percent relative standard deviation (%RSD) of the relative response factor (RRF), which is calculated as

$$RRF = A_x C_{is}/(A_{is} C_x) \qquad (1)$$

where A_x and A_{is} are abundances of the target ions for the target compound and internal standard, respectively, and C_{is} and C_x are concentrations of the internal standard and target compound in the calibration standard, respectively (µg m^{-3}). Based on US EPA guidance,[11] this approach provides a more robust analysis than simpler procedures, *e.g.*, using the fit (R^2) of the calibration line.

Recovery/desorption efficiency. Recoveries for each VOC were evaluated as the fraction of the mass recovered from the sorbent compared to that injected into the sorbent tube. Injection mass determinations were based on GC-MS calibrations by removing the desorber system from the GC (see below), and using 2 µl injections of the 10 ng µl^{-1} standard, performed in triplicate. Most analyses were performed within 1 d (and generally within 3 h) after spiking the tube.

Storage tests. These experiments were designed to investigate the stability of loaded tubes. In these tests, 9 tubes were loaded with 20 ng per tube of each VOC, equivalent to an intermediate air concentration of 6.7 µg m^{-3} assuming a 3 l air sample. Three tubes were analyzed immediately. The others were capped, wrapped in clean aluminium foil, placed in a clean (previously baked) glass jar, and stored at 4 °C. Three tubes were analyzed after a storage period of 1 week, and 3 tubes after 6 weeks of storage. Storage losses at 1 and 6 weeks were calculated as the fraction of the concentration measured in the tubes that were analyzed immediately after loading. This approach helps to separate storage losses from incomplete recovery of VOCs (evaluated as recovery/desorption efficiency).

Humidity tests. The final set of laboratory tests evaluated the recoveries and other aspects of system performance under high humidities. Three tubes were first exposed to 4 l of 49% RH clean air, and 3 others to 88% RH air, using the method described earlier. Tubes were then spiked with 2 µl of the 10 ng µl^{-1} standard (as described earlier) and analyzed on the same day.

Field studies

Ambient air quality and commuter exposure. The first field study was designed to estimate VOC exposures of commuters in commercial, residential and industrial areas in Detroit, Michigan, a city of ~1 000 000. Ambient air samples were collected along roadways and in vehicles during morning (7–10 a.m.) and afternoon (2–5 p.m.) "rush hour" periods on 4 consecutive Wednesdays in October and November, 1999. During the sampling, temperatures ranged from 1 to 20 °C, and slight precipitation was recorded on 2 days. This paper reports on only 16 duplicate samples and blanks taken in this study. (Study details are presented in Batterman *et al.*[12]) Duplicate samples were collected using personal sampling pumps (PCXR7 SKC, Eighty-Four, PA, USA) and twin proportioning valves (MSA, Pittsburgh, PA, USA) connected to stainless-steel connectors to which the sorbent tubes were attached. In the field, personnel (instructed to wear latex gloves) picked a clean sorbent tube from a glass storage container, removed the end caps, installed the tube into the sampling system, started the pump, and recorded pertinent information. When sampling was completed, the pump was shut-off, the time recorded, and the sorbent tube was unscrewed from the sampler, capped, wrapped in clean foil, placed in a polyethylene bag, and stored in a glass jar. Sample flow rates, nominally 20 ml min^{-1}, were measured using a bubble meter at the beginning and end of each sample, and the average was used to estimate the sample volume (typically 3–5 l). In the laboratory, samples were stored at 4 °C and analyzed within 1–3 days of collection. One or several field blanks were used each sampling day. Blanks were treated like the other tubes, *i.e.*, they were taken to the field, briefly opened, capped, stored with the other samples, and analyzed.

The agreement between duplicate samples in the commuter field study (as well as the indoor air study described below) was determined by calculating the analytical precision P (%) as

$$P = |C_1 - C_2|/C \times 100\% \qquad (2)$$

where C_1, C_2 and C are concentrations of replicates 1 and 2, and their average, respectively.

Indoor air quality in an office building. The second field study measured VOC levels in a mid-sized five-story office building located near the center of Ann Arbor, Michigan, a city of ~100 000. While not a "problem" building, occasional paint fumes, truck odors, and overheating have been noted by occupants. Each floor of this building has a separate variable air volume (VAV) air handling system that shares a common air intake and relief. The activities on each floor are similar, predominately clerical and computer-oriented. Samples were collected in the occupied building from 9 a.m. to 3 p.m. on subsequent Wednesdays. This paper reports on 15 duplicate measurements that were collected over a 4 week period in February and March, 2000. (Additional details are presented by Godwin *et al.*[13])

In brief, duplicate VOC samples were collected at centrally located areas on three floors of the building at breathing height (1.5 m). Sorbent tubes were screwed onto stainless-steel connectors connected using polyethylene tubing to a pneumatic flow controller, rotameter, and 120 V pump. Separate flow systems (but sharing the same pump) were used to take side-by-side samples. Flows were set to a nominal 10 ml min^{-1}, and measured using a bubble meter at the beginning and end of each sampling period. As before, the average flow rate was used to estimate the sample volume. The handling and storage of sorbent tubes followed procedures described earlier.

Sample analysis, calibration and quality control

Desorption. Air samples were analyzed using an automated short-path thermal desorption/cryofocusing system (Model 2000, Scientific Instrument Services) that sits directly on the injector/septum area of the gas chromatograph/mass spectrometer (GC/MS, Model 6890/5973 running Chemstation, G1701BA, Version B.01, Hewlett-Packard, Palo Alto, CA, USA). The liquid N$_2$ cooled cryofocus trap is mounted in the GC oven, just below the injection port and around a short (5 cm) section of the capillary column. A small outboard power supply/controller unit is mounted along side the GC. This system has the capability of automatically and sequentially analyzing 12 sorbent tubes, and features programmable times, temperatures and/or temperature ramps for purge, desorption, focusing, and injection modes. For syringe injections (or septum replacement), the desorber unit is simply lifted off the GC and placed elsewhere; no valves or switches are needed.

For analysis, a sorbent tube is removed from the refrigerated storage container and sealing caps are removed. In desorption, gas flow directions are reversed from sampling. The downstream side of the sorbent tube is screwed on to a stainless-steel connector, which contains a check valve and a small VOC trap. The upstream side of the tube is screwed onto a previously cleaned (by heating to 325 °C under a helium flow in the conditioning oven) 3.5 cm long stainless-steel side-port needle. Sealing is provided using integral graphitized Vespel® seals (Scientific Instrument Services) at both ends of the sorbent

Table 2 Operating conditions for automated thermal desorption system and GC-MS

|		
Thermal Desorption	Dry purge flow rate	40 ml min^{-1}
	Dry purge time	1 min
	Inject time	1 min
	Desorption temperature	200 °C
	Desorption flow rate	10 ml min^{-1}
	Desorption time	5 min
	Guard column	None
	Cryo trap temperature	−140 °C
	Cryo heat delay	0.3 min
	Cryo heat temperature	250 °C
	Cryo heat time	5 min
GC-MS	Injector	Split, temperature at 230 °C, split ratio 10 : 1
	Column	HP-5MS, 5% phenylmethyl siloxane, 30 m × 0.25 mm (id), 0.25 μm film thickness
	Flow rate	1 ml min^{-1} = 35 cm s^{-1}
	Temperature program	−10 °C hold for 3 min
		8 °C min^{-1} to 20 °C, hold for 3 min
		5 °C min^{-1} to 120 °C, hold for 1 min
		20 °C min^{-1} to 250 °C, hold for 1 min
		Total run time 38.25 min
	Mass mode and range	Scan mode, 29–270 u, 3 scan s^{-1}, 0.1 u step size
	MS quad temperature	150 °C
	MS source temperature	230 °C
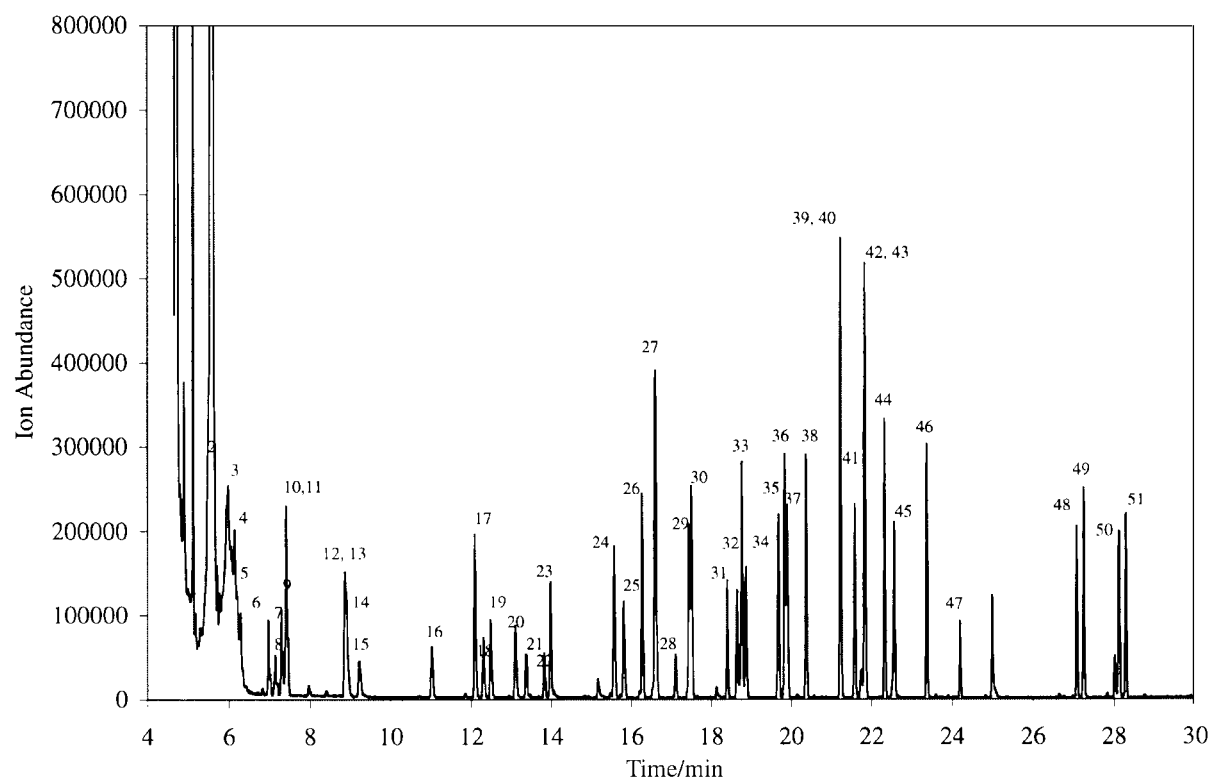
Fig. 1 Total ion chromatogram for a loaded sorbent tube containing 2 ng each for aromatic and halogenated compounds. The tailing of the solvent can be observed in the chromatogram up to about 5.5 min. Refer to Table 5 (see later) for peak identification.

tube. The sorbent tube assembly is then placed on the desorber's carousel. Up to 12 of these assemblies can be accommodated on the carousel.

The automated desorption analysis proceeds through the following steps (Table 2). First, a particular tube is selected, and the cryofocusing trap is cooled to −140 °C. After achieving the desired GC oven, heater block, and cryofocus temperatures, excess water on the sorbent tube is removed using a dry purge (~40 ml min⁻¹ of GC carrier gas helium for 1 min). The tube assembly is then pneumatically lowered so that the desorption needle pierces the GC septum, and the carrier gas is diverted through the tube and into the GC column inlet. The GC's electronic pressure control (EPC) is used to maintain the desired split ratio (10 : 1). The desorber system does not alter EPC functioning. Before proceeding further, a pressure check is made to ensure that the system is leak-tight. After a 1 min equilibration, heater blocks are positioned around the tube. VOCs desorbed from the tube then follow a "short path" through the needle and are collected in the cryotrap at the front of the GC column. This short path design minimizes carry-over from sample-to-sample, since each tube has its own desorption needle, as well as delays, losses and artifacts that can result with long transfer lines. After 5 min desorption, the sample is removed from the GC flow path and the cryofocusing trap is rapidly heated (⩽10 s) to 250 °C, providing a narrow injection band that enhances separation and resolution of compounds. The GC program is then started.

GC-MS analysis. The GC was equipped with a 30 m × 0.25 mm id column with 0.25 μm film thickness (HP-5MS, Hewlett-Packard, Santa Clarita, CA, USA). Carrier gas was ultra-high (99.999%) purity helium (Cryogenic Gases, Detroit, MI, USA), cleaned using a heated catalytic gas purifier (Supelco, Bellefonte, PA, USA) and a fresh trap (HP, Santa Clarita, CA, USA). GC-MS parameters, optimized for the target compounds, are shown in Table 2. The run time for sample analysis, including desorption (7 min), and GC analysis (38 min) was 45 min.

Compounds were identified using target ions, qualifier ions and retention time. Quantification was based on the ratio of the target ion of the target compound (Table 1) to ion $m/z = 96$ of the internal standard fluorobenzene and ion $m/z = 174$ of p-bromofluorobenzene. Two internal standards were used, namely, fluorobenzene for compounds eluting in the first 13 min and p-bromofluorobenzene for the remainder, which improves accuracy given the relatively long analysis time. The GC software was setup to automatically identify and quantify target compounds in samples.

Fig. 1 shows a typical chromatogram from a loaded low concentration sorbent tube (2 ng of each VOC). The optimized method provides excellent peak shape and good separation of all target compounds.

Quality control. The GC/MS was tuned daily using perfluorotributylamine to help maximize instrument sensitivity. Following tuning, a bake-out procedure was used to ensure the cleanliness of the system. In this 31 min procedure, desorption blocks were heated to 300 °C, the injector was at 325 °C, the MS detector transfer line was set to 300 °C, and the GC temperature program started at 250 °C for 15 min, ramped at 10 °C min⁻¹ to 310 °C, and was held for 5 min. A daily calibration/quality control sample was then run, using a freshly-loaded sorbent tube containing 20 ng of each aromatic and halogenated compound. The difference between the daily RRF and the calibration RRF (from the 5 point calibration) was required to be within 30%. Finally, a blank tube was run prior to the analysis of any sample. Concentrations of any target compound in the blank should not (and did not) exceed the method limit of three times the MDL.

Results and discussion

Laboratory performance evaluation

Blanks. Blank emissions from dry tubes included toluene and benzaldehyde, and less frequently, benzene, α-methylstyrene, phenol, 1,5-dimethyl-3,3-diphenyl-2-pyrrolidinone, non-

Table 3 Average emissions (ng per tube) for freshly cleaned tubes, stored tubes, humidified blanks and field blanks[a]

	Compound	Freshly cleaned	1 week storage	6 week storage	Humidified blanks[b]	Field blanks Ambient	Field blanks Indoor air
Target compounds	Benzene	0.95 (1)	—	—	—	—	—
	Toluene	0.56 (5)	0.47 (1)	0.64 (3)	0.53 (4)	0.44 (2)	0.22 (6)
	Phenol	2.57 (1)	—	1.58 (3)	—	—	—
	1,4-Dichlorobenzene	—	—	—	—	42.96 (1)	—
	Limonene	—	—	—	—	—	1.47 (1)
Non-target compounds[c]	Acetone	—	—	—	24.18 (3)	—	—
	2-Pentanone	—	—	—	0.30 (1)	—	—
	Benzaldehyde	0.61 (2)	0.54 (1)	0.54 (2)	0.89 (4)	0.57 (2)	0.83 (2)
	α-Methylstyrene	—	0.01 (1)	0.16 (3)	0.52 (4)	—	1.07 (4)
	Benzonitrile	—	—	—	—	5.11 (1)	—
	Octanal	—	—	—	0.08 (2)	—	—
	1,5-Dimethyl-3,3-diphenyl-2-pyrrolidinone	0.29 (1)	0.25 (2)	—	—	0.16 (1)	0.17 (1)
	2-pyrrolidinone	—	—	—	—	—	—
	Nonanal	—	1.51 (1)	2.65 (2)	0.64 (1)	0.87 (2)	—
	6-Bromo-1-hexane	0.39 (2)	0.50 (1)	—	0.34 (2)	—	0.12 (4)
	3-Phenyl-2-propenal	—	—	—	1.45 (2)	—	—
Sample size		14	3	3	9	4	7

[a]Numbers in parentheses show number of blanks where emissions exceeded MDLs (shown in Table 4, see later). [b]Water blanks include 5 tubes prepared at 49% RH and 4 tubes prepared at 88% RH. [c]Non-target compounds were quantified by the response factor of 1,2,3-trichloropropane.

anal and 6-bromo-1-hexene (Table 3). Quantities of these compounds ranged from 0.3 to 2.6 ng per sorbent tube, corresponding to 0.1–0.9 µg m^{-3} in a 3 l air sample. Emissions of α-methylstyrene and nonanal increased from tubes stored for 1 and 6 weeks, possibly due to sorbent degradation. Overall, blank emissions were below 0.3 ng per sorbent tube for all target compounds except benzene, toluene, and phenol. Humidified blanks had similar or sometimes larger emissions of toluene, benzaldehyde, α-methylsytrene, nonanal and 6-bromo-1-hexene, as well as emissions of several non-target compounds, e.g., acetone, 2-pentanone and 3-phenyl-2-propenal. On three occasions, the quantity of acetone was significant.

Field blanks showed comparable emissions of toluene, benzaldehyde, α-methylstyrene, 1,5-dimethyl-3,3-diphenyl-2-pyrrolidinone, nonanal, and 6-bromo-1-hexene (Table 3). However, larger emissions were found for 1,3-dichlorobenzene in an ambient blank and limonene in an indoor blank. These may be due to diffusion into sorbent tubes when mimicking the sampling procedure or incomplete conditioning. In general, however, emissions of target compounds were well below 0.5 ng per sorbent tube, indicating negligible contamination from sample handling and transportation.

Blank emissions during thermal desorption of Tenax and other adsorbents have been previously detected[3,5,14] and can arise from several sources. Artifact formation due to degradation of the sorbent is the likely source of the aromatic compounds.[15] Possible sources of aldehydes and long chain alkanes, which were found at low levels in the blanks, include reactions with water, incomplete conditioning of the tube, contamination from the carrier gas, contamination of the upstream flow path of the cryotraps, and permeation of contaminants in laboratory air through the flexible tubing used for carrier gas. (Copper tubing is used internally in the desorber system, but Teflon tubing was used externally to connect the system.) In addition, stored tubes may become contaminated due to the presence of VOCs in the storage environment and permeation through tube seals, or off-gassing from the Teflon tube seals. The origin of acetone is unknown. The intermittent appearance of low level contamination suggests that the blank emissions might result from degradation of the Tenax GR sorbent and incomplete conditioning of the sorbent tubes.

Overall, the system met TO-17 method performance criteria[3] that specify an MDL ⩽0.5 ppb (corresponding to a mass limit of 6.1 ng per sorbent tube) assuming a 3 l air sample. Blank emissions were negligible for most compounds with the exception of acetone.

Internal standard. Abundances of the two standards were within 40% (the guideline specified by US EPA[10]) of the mean abundance measured during the initial calibration. On average, reproducibilities over the calibration range for fluorobenzene and p-bromofluorobenzene were 19.9% and 14.8%, respectively. For the 29 daily calibrations performed over 4 months, all abundances of fluorobenzene were within 40% of the calibration mean, and all but four for p-bromofluorobenzene.

Method detection limit. Based on a sampling volume of 3 l, MDLs for all target compounds were below 0.5 ppb and most were well below 0.2 ppb (Table 4). Phenol and nitrogen containing compounds showed higher MDLs (>0.2 ppb) due to the lower sensitivity of the MSD detector for these compounds.[16] In addition, the non-polar column used in this study, which tends to broaden peaks of polar compounds, somewhat impaired integration. Greater sensitivity can be attained using higher sampling volumes, more sensitive detectors (such as electron capture) or optimizing the MSD sensitivity using a narrow u range, decreasing the split ratio, and by using a pulsed split mode for injection. Still, the method easily met the 0.5 ppb MDL requirement for ambient air sampling.[3]

Reproducibility. Table 4 shows experimentally-determined reproducibilities as the average RSD across the concentrations used in the calibration, as well as the range of RSDs. The determination was based on triplicate or quadruplicate analysis at 5 concentrations. Most VOCs had RSDs that averaged from 5 to 15%. Reproducibilities were slightly lower for 1,1-dichloroethane, 2-butanone, 2,2-dichloropropane, 2-hexanone, phenol, o-cresol, and m/p-cresol (RSDs between 20 and 30%). Several of these VOCs eluted within the first 6 min, and the lower reproducibility is partly attributable to interference from the solvent peak. This would not be an issue in air sampling since solvents are not used. Reproducibilities are also lower for phenols, ketones and nitrogen-containing compounds for which the MSD is less sensitive.

As expected, RSDs increase as the concentrations approach MDLs.[2,4,17] At higher concentrations (e.g., 40 ng per tube), reproducibilities were excellent, within a few percent. The

Table 4 Retention time (RT); method detection limit (MDL); reproducibility; linearity as RSD of relative response factor, and desorption efficiency (DE) for target compounds measured in laboratory tests

Compound	RT/min	MDL µg m⁻³	MDL ppb	Reproducibility, RSD (%) Average	Min	Max	Linearity (%)	DE[a] (%)
1,2-Dichloroethylene (*trans,E*)	4.82	0.449	0.113	15.0	1.5	35.4	26	64
tert-Butyl methyl ether	5.18	0.383	0.109	10.4	3.2	15.0	10	72
1,1-Dichloroethane	5.24	0.158	0.039	27.5	3.6	58.9	21	76[b]
Propanenitrile	5.43	0.649	0.288	12.4	4.8	22.1	10	278[b]
Methacrylonitrile	5.98	0.382	0.139	12.7	8.8	18.1	10	51
1,2-Dichloroethylene (*cis, Z*)	6.03	0.115	0.029	20.7	1.3	40.8	10	83
2-Butanone	5.97	0.434	0.147	25.7	12.9	45.2	24	70
2,2-Dichloropropane	6.19	0.195	0.042	29.0	13.1	47.9	23	44
Bromochloromethane	6.24	0.267	0.050	19.3	3.0	52.8	24	102
Chloroform	6.33	0.093	0.019	9.8	2.4	29.0	7	92
Methyl acrylate	6.48	0.476	0.135	8.3	4.1	10.9	9	66
Tetrahydrofuran	6.76	0.543	0.184	12.1	6.1	24.0	23	121
1,1,1-Trichloroethane	7.01	0.119	0.022	13.1	6.5	19.0	15	75
1,2-Dichloroethane	7.19	0.071	0.018	17.6	6.0	27.4	14	82
Butyl chloride	7.25	0.314	0.083	10.8	1.7	18.7	13	92
1,1-Dichloropropene	7.33	0.062	0.014	10.1	2.3	29.0	12	102
Benzene	7.45	0.097	0.030	12.0	1.8	29.0	20	112
Carbontetrachloride	7.46	0.106	0.017	14.9	5.9	37.0	11	92
Chloroacetonitrile	8.74	0.304	0.098	10.6	1.2	15.5	12	90
1,2-Dichloropropane	8.89	0.110	0.024	8.8	0.3	20.6	17	110
Trichloroethylene	8.91	0.055	0.010	10.4	0.7	28.0	13	113
Dibromomethane	8.96	0.055	0.008	11.9	0.3	22.9	20	108
2-Nitropropane	9.27	0.975	0.268	10.9	7.2	17.2	15	106
Bromodichloromethane	9.26	0.115	0.017	8.3	0.4	18.7	18	109
Methyl methacrylate	9.93	0.296	0.072	7.1	1.9	11.3	2	124
1,1-Dichloro-2-propanone	10.72	0.246	0.047	20.3	9.9	30.0	10	51
1,3-Dichloropropene (*cis, Z*)	11.05	0.093	0.020	9.6	0.4	20.2	21	112
Isobutyl methyl ketone	11.37	0.401	0.098	17.1	3.8	34.4	16	94
Toluene	12.12	0.135	0.036	8.2	2.7	15.7	21	128
1,3-Dichloropropene (*trans, E*)	12.33	0.083	0.018	9.2	0.9	18.2	29	120
1,1,2-Trichloroethane	12.51	0.129	0.024	5.9	1.6	10.7	21	122
1,3-Dichloropropane	13.12	0.063	0.014	6.8	0.4	12.3	18	127
Dibromochloromethane	13.40	0.102	0.012	7.0	1.7	9.7	12	84
Ethyl methacrylate	13.58	0.000	0.000	9.7	2.4	16.9	12	UD
2-Hexanone	13.64	0.129	0.032	21.8	6.2	36.0	9	74
1,2-Dibromoethane	13.84	0.066	0.009	7.6	0.7	10.8	8	83
Tetrachloroethene	14.00	0.035	0.005	6.1	1.1	11.7	11	87
Chlorobenzene	15.59	0.023	0.005	4.5	0.9	8.8	9	95
1,1,1,2-Tetrachloroethane	15.83	0.042	0.006	7.4	1.9	12.9	11	97
Ethylbenzene	16.30	0.020	0.005	6.4	0.5	11.5	9	97
p-Xylene, *m*-xylene	16.63	0.007	0.002	8.9	0.8	13.2	10	105
Bromoform	17.13	0.181	0.018	10.7	1.7	18.2	27	94
Styrene	17.46	0.034	0.008	9.9	0.4	16.6	17	98
o-Xylene	17.53	0.012	0.003	8.9	1.3	13.1	10	103
1,1,2,2-Tetrachloroethane	18.41	0.037	0.005	7.3	0.6	14.9	10	103
1,2,3-Trichloropropane	18.66	0.040	0.007	11.2	2.1	25.3	9	100
Isopropylbenzene (cumene)	18.79	0.010	0.002	7.5	1.0	13.9	12	107
Bromobenzene	18.89	0.025	0.004	8.2	1.0	16.4	12	102
1,4-Dichloro-2-butene (*trans, E*)	19.05	0.459	0.090	16.4	3.5	31.6	31	85
a-Pinene (1*R*)-(+)	19.08	0.023	0.004	11.2	5.7	22.9	14	UD
2-Chlorotoluene	19.69	0.017	0.003	7.8	0.4	16.2	10	103
n-Propylbenzene	19.89	0.012	0.002	8.1	0.6	17.4	12	100
4-Chlorotoluene	19.91	0.017	0.003	8.9	0.6	17.9	11	104
1,3,5-Trimethylbenzene	20.38	0.014	0.003	8.2	0.2	16.9	14	105
Pentachloroethane	20.58	0.144	0.017	6.6	1.0	14.4	6	92
Phenol	21.09	1.247	0.324	33.3	22.3	41.7	33	85
tert-Butylbenzene	21.24	0.013	0.002	8.1	1.5	15.9	13	114
1,2,4-Trimethylbenzene	21.24	0.020	0.004	9.5	0.7	20.8	12	108
1,4-Dichlorobenzene	21.59	0.022	0.006	9.3	1.1	20.5	11	106
1,3-Dichlorobenzene	21.84	0.032	0.005	9.5	1.2	21.1	12	111
sec-Butylbenzene	21.85	0.034	0.006	8.9	0.5	20.0	13	113
p-Isopropyltoluene	22.34	0.020	0.004	9.7	1.2	21.5	17	108
Limonene (*R*)-(+)	22.46	0.100	0.018	12.0	3.0	42.0	24	UD
1,2-Dichlorobenzene	22.58	0.011	0.002	9.9	1.3	21.9	12	107
n-Butylbenzene	23.38	0.040	0.007	10.3	0.3	24.0	19	108
o-Cresol	23.43	0.996	0.225	28.0	18.5	41.1	38	75
Hexachloroethane	23.83	0.240	0.025	7.1	3.2	12.1	9	112
m-Cresol, *p*-cresol	24.09	1.717	0.388	26.1	11.8	49.8	41	87
1,2-Dibromo-3-chloropropane	24.21	0.139	0.014	12.3	2.2	28.0	32	101
Nitrobenzene	24.34	0.417	0.083	14.1	2.4	20.6	53	58
1,2,4-Trichlorobenzene	27.09	0.059	0.008	11.4	2.1	26.3	18	108
Naphthalene	27.26	0.055	0.006	10.5	1.5	23.1	21	114
1,2,3-Trichlorobenzene	28.13	0.040	0.005	10.5	1.2	25.1	18	109
Hexachlorobutadiene	28.30	0.040	0.004	9.3	1.6	22.5	19	101
Mean		0.198	0.049	12.0	3.2	23.3	16	99
Standard deviation		0.299	0.080	6.0	4.1	11.1	9	28

[a]UD means undetermined. [b]Peak is too broad to integrate accurately.

Table 5 Recovery rates (in %) for aromatic and halogenated compounds for stored samples and humidified samples[a]

ID	Compounds	Stored samples		Humidified samples[b]	
		1 week	6 week	50% RH	90% RH
1	1,2-Dichloroethylene (trans, E)	93	58[c]	84	60
2	1,1-Dichloroethane	71	74	106	113
3	1,2-Dichloroethylene (cis, Z)	119	125	127	107
4	2,2-Dichloropropane	77	63	77	84
5	Bromochloromethane	96	74[c]	119	96
6	Chloroform	93	81[c]	106	99
7	1,1,1-Trichloroethane	89	89	128	126
8	1,2-Dichloroethane	101	103	112	98
9	1,1-Dichloropropene	87	90	100	89
10	Benzene	88	86	102	98
11	Carbontetrachloride	97	96	108	111
12	1,2-Dichloropropane	90	79[c]	103	97
13	Trichloroethylene	95	92	87	80
14	Dibromomethane	89	90	86	77
15	Bromodichloromethane	87	98	93	88
16	1,3-Dichloropropene (cis, Z)	89	86	92	86
17	Toluene	94	86	91	91
18	1,3-Dichloropropene (trans, E)	83	81	86	85
19	1,1,2-Trichloroethane	92	80	92	90
20	1,3-Dichloropropane	92	80	91	90
21	Dibromochloromethane	89	107	98	90
22	1,2-Dibromoethane	83	95	82	74
23	Tetrachloroethylene	84	100	115	106
24	Chlorobenzene	83	90	119	114
25	1,1,1,2-Tetrachloroethane	86	101	109	106
26	Ethylbenzene	83	89	118	116
27	p-Xylene, m-xylene	81	88	114	112
28	Bromoform	90	107	103	102
29	Styrene	78	81	108	108
30	o-Xylene	82	88	114	113
31	1,1,2,2-Tetrachloroethane	84	82	117	116
32	1,2,3-Trichloropropane	84	84	119	117
33	Isopropylbenzene	82	84	106	106
34	Bromobenzene	83	88	117	115
35	2-Chlorotoluene	82	86	111	111
36	Propylbenzene	82	83	99	102
37	4-Chlorotoluene	81	85	114	111
38	1,3,5-Trimethylbenzene	82	83	106	106
39	tert-Butylbenzene	83	83	103	98
40	1,2,4-Trimethylbenzene	82	81	107	109
41	1,4-Dichlorobenzene	81	82	103	105
42	1,3-Dichlorobenzene	81	83	103	104
43	sec-Butylbenzene	82	81	107	105
44	p-Isopropyltoluene	81	79	106	105
45	1,2-Dichlorobenzene	82	80	104	105
46	n-Butylbenzene	81	80	110	111
47	1,2-Dibromo-3-chloropropane	85	86	100	101
48	1,2,4-Trichlorobenzene	83	79	99	94
49	Naphthalene	80	86	104	96
50	1,2,3-Trichlorobenzene	84	79	100	92
51	Hexachlorobutadiene	85	74	94	88
	Mean	86	87	104	100
	Standard deviation	7	10	11	13

[a]Sample size of 3 for each condition. [b]Humidified samples were analyzed immediately after preparation. [c]Statistically significant differences ($P < 0.05$) between samples analyzed immediately and samples stored for 6 weeks. No statistically significant differences were found for samples stored for 1 week.

reproducibility determinations included the error in loading the tube, which is estimated as approximately 5%, as well as variation in desorption efficiency, cryotrapping, GC-MS analysis, *etc.* Overall, the result show excellent reproducibility, well within the 20% required for ambient air sampling. Such precision is made possible by well-controlled automation of the critical steps in sample analysis.

Linearity. Table 4 shows the linearity results for the 5 point calibrations performed for each VOC. For most compounds, the %RSD of the RRF was below 30%, indicating a high degree of linearity over the concentration range tested. However, phenols, some chlorinated compounds and nitrobenzene

showed somewhat higher RSDs, up to about 50%. Again, the lower sensitivity of the MSD detector for these compounds and non-polar column tends to decrease linearity for these compounds.

Desorption efficiency. Recovery rates for most compounds ranged between 80 and 120% (Table 4). However, two early eluting compounds showed impossibly high recovery rates, *i.e.*, propanenitrile (278%) and bromochloromethane (329%). This is probably a result of cryofocusing, which narrows the peak and enhances the resolution compared to the broader calibration peaks that were based on direct (liquid) injections without focussing. The "shoulders" of these broader peaks

Table 6 Results for ambient air study, based on 16 pairs of replicates (32 tubes in total)

	Concentration/µg m^{-3}			Precision (%) Mean	Percent within precision limit[a]	
	Mean	Min	Max		⩽20	⩽50
Benzene	6.07	0.17	13.61	35	57	71
Carbontetrachloride	0.29	0.22	0.35	48	0	100
Toluene	12.99	0.14	41.62	35	38	81
Tetrachloroethylene	0.60	0.04	1.81	45	50	63
Ethylbenzene	2.51	0.62	7.68	29	46	85
p-Xylene, *m*-xylene	8.24	2.00	25.20	29	31	85
Styrene	0.98	0.22	3.14	43	31	69
o-Xylene	2.76	0.72	8.40	25	38	92
Isopropylbenzene	0.28	0.11	0.51	61	33	67
Propylbenzene	1.03	0.16	2.81	34	56	67
1,3,5-Trimethylbenzene	1.39	0.46	4.09	26	38	92
Phenol	1.14	0.97	1.30	28	0	100
1,2,4-Trimethylbenzene	4.70	1.71	13.13	23	46	92
1,3-Dichlorobenzene	1.13	0.11	2.93	70	11	33
p-Isopropyltoluene	0.36	0.10	0.76	83	33	33
n-Butylbenzene	0.59	0.09	2.26	73	14	29
Naphthalene	1.40	0.18	4.35	46	23	69
Mean				43	32	72

[a]The percentage for analytical precision within certain limit (*e.g.*, 20% or 50%).

were not fully integrated. By manually integrating the shoulders, the desorption efficiency of bromochloromethane was re-estimated as 102%. However, the propanenitrile peak was too broad to integrate accurately.

Low recovery rates (<80%) might be explained by several reasons. First, low boiling point (<60 °C) compounds, *e.g.*, 1,2-dichloroethylene, *tert*-butyl methyl ether and 1,1-dichloroethylene, may break through the cryotrap. This is indicated in the much lower recoveries of these and some other compounds found for a warmer trap temperature (–100 °C compared to the –140 °C used in this study). Second, the desorption temperature (200 °C) may not have been high enough to break the bonds between light compounds that might have been trapped in Carbosieve SIII (after breaking through the Tenax GR). Desorption and conditioning temperatures in multi-sorbent systems are restricted by the sorbent with lower maximum temperature. Of the sorbents used here, Tenax GR has a maximum temperature of 350 °C, while Carbosieve SIII is limited to 400 °C. Increasing the desorption temperature from 200 to 250 °C did not improve desorption efficiency. Instead, the higher temperature tended to broaden the peaks of early eluting compounds, a possible result of a slightly warmer and thus less efficient cyrotrap. Third, several chlorinated compounds and nitrogen or oxygen containing compounds have a relatively high affinity with Tenax GR, due to hydrogen-bond interactions, making desorption less efficient.[18]

Carry-over. All blanks analyzed after high concentration samples were clean (no peaks of target compounds were detected). Thus, it is evident that the short-path system using separate flow paths avoided any residual carry-over from previous samples.

Storage stability. Storage tests used aromatic and halogenated compounds, in part because they are more frequently found in air sampling. Storage of loaded sorbent tubes for 1 and 6 weeks prior to analysis caused small losses (Table 5). Across the 51 compounds tested, recoveries averaged 86±7% and 87±10% for 1 and 6 week storage periods, respectively, as compared to the tubes analyzed immediately after loading. Thus, on average, a 14% loss occurred during the first week of storage after which no further loss resulted, however, the variability of losses did slightly increase. Using a paired *t*-test, statistically significant ($p \leqslant 0.05$) losses between samples analyzed immediately after preparation and samples stored
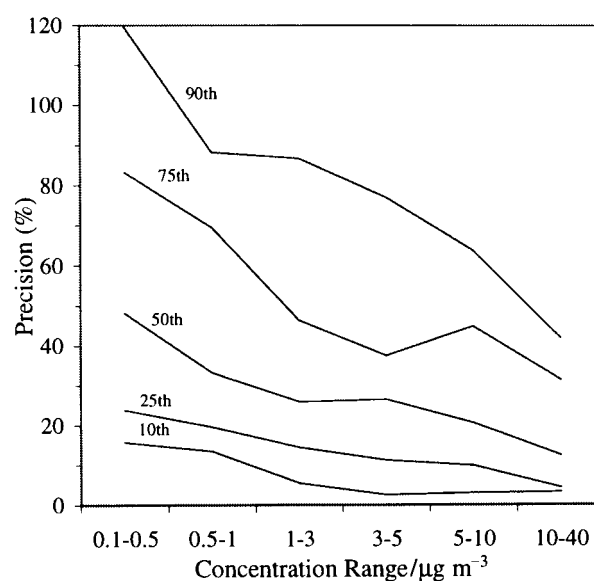

Fig. 2 Analytical precision for 16 replicates and 18 compounds (shown in Table 6) *versus* mean concentration measured in the ambient air quality study (lines indicate percentiles of analytical precision; the figure is based on 162 pairs of replicates)

for 6 weeks were found for 4 compounds (1,2-dichloroethylene, bromochloromethane, chloroform and 1,2-dichloropropane). Still, losses for most of those high boiling point compounds were not large, indicating that the samples remain stable when appropriately stored (refrigerated in a VOC-free environment). Of course, samples should be analyzed as soon as possible after collection to minimize the potential for losses and sample degradation.

Humidity effects. The same 51 aromatic and halogenated compounds were used in the humidity tests. Only small differences were found in the recoveries of VOCs on dry tubes and tubes preconditioned with 4 l of 49% RH air (Table 5). However, tubes preconditioned with 4 l of 88% RH air displayed several chromatography problems, *i.e.*, elution times shifted, peak width increased, and 2 breakdown peaks were formed for benzene. Inconsistency in elution times was the main problem with the high humidity condition. For compounds eluting before toluene, elution times could be
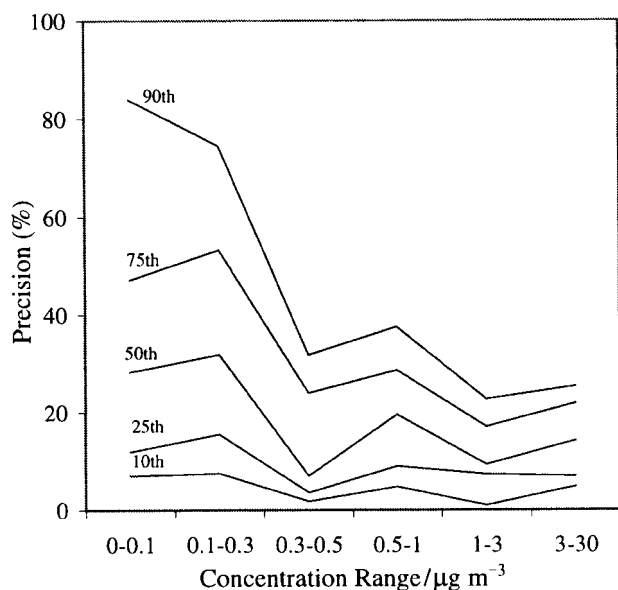
Fig. 3 Analytical precision for 15 replicates and 18 compounds (shown in Table 7) *versus* mean concentration measured in the indoor air study (lines indicate percentiles of analytical precision; the figure is based on 143 pairs of replicates)

delayed up to 0.7 min, making identification difficult since the automatic integration/identification program often failed, and compound identification required time consuming manual searches of target and qualifier ions. Such shifts will cause identification errors with non-specific detectors (flame ionization, photo-ionization detector, *etc.*) that depend solely (or largely) on retention times for identification.

VOC recoveries for the humidified tubes averaged $104 \pm 11\%$ and $100 \pm 13\%$ for 49% and 88% RH samples, respectively, comparable to that obtained for dry tubes (Table 5). In no case did the on-column cryofocus trap become blocked. The trap volume is approximately 2.5 µl, based on a 5 cm long trap and a column id of 0.25 mm. An 88% RH 4 l air sample contains 72 µl water, far exceeding the trap volume. However, most water is excluded since the selected sorbents were relatively hydrophobic, a portion of water collected on the sorbent was removed by the dry purge, and the sample was split 10:1. Additionally, a water plug will freeze out as an elongated volume,[7] rather than a cylinder or sphere in the trap. Water trapped on the capillary cryotrap did not appear to restrict flow or change the split ratio, which is regulated by the GC's electronic pressure control, based on examination of absolute ion abundances and a comparison of the time needed to heat the trap (<10 s) and the delays in elution time. In summary, the method could accommodate sample volumes of 3 l without problems due to water vapor.

In many environmental applications, water vapor is present at high levels (water vapor saturation at 20 °C is 17.3 g m^{-3} or 2.3%), exceeding (sub-ppb) concentrations of target compounds by 10^8 times. Several water management techniques can be used to manage the adverse effects of water.[3,7,10] First, hydrophobic sorbents are generally used with direct thermal desorption methods. The selection, quantity and use of adsorbents involves many considerations. The dual sorbent bed used here combines Tenax GR, which has low affinity for water, with a smaller amount of carbon molecular sieve, which is moderately hydrophilic. The elimination of water prior to analysis will increase efficiency of the analysis. Second, the initial desorption step used a short dry purge of helium to help remove some excess water. It should be noted that the short-path desorber system used here provides a reverse flow of dry gas through the sorbent, in contrast to the forward flow (sampling direction) suggested by US EPA.[3] (Forward flows can be provided off-line.) Third, sample splitting can be used to

reduce collected water, but this reduces sensitivity. Other water management techniques, *e.g.*, water permeable membranes,[19] or gradually heating of the trap to drive off water,[20] are available but are not generally used with thermal desorption techniques. The desorber system has the capability to slowly "ramp up" the tube temperature in the desorption cycle, which could also provide the ability to drive off water. This may be considered as a water management technique if cryofocusing is not required.

Field studies

Ambient air study. Table 6 summarizes the results of the commuting study for those VOCs where average concentrations exceeded 0.3 µg m^{-3}. A number of fuel related aromatic compounds (benzene, toluene, xylene, *etc.*) were detected at low to moderate concentrations (<42 µg m^{-3}). Several chlorinated compounds (tetrachloroethylene and 1,3-dichlorobenzene) were found at lower levels (<3 µg m^{-3}), possibly due to industrial emissions. Concentrations of most VOCs considerably exceeded those measured as 24 h averages in 5 years of sampling at several fixed monitoring sites in Detroit using whole air (canister) sampling and US EPA method TO-14.[10] This is not unexpected since samples were taken along busy roads at peak commuting times. Sorbent tube sample volumes were 3–6 l and light rain fell on two of the four sampling days, thus some adverse effects of water are expected based on the laboratory results presented earlier.

The analytical precision among 16 pairs of replicates and 17 compounds (total of 162 measurement pairs) averaged 39%. When compounds measuring <1 µg m^{-3} are excluded, precision improved to an average of 31%. These statistics represent the average, but not the variability, in precision determinations. Fig. 2 presents a useful analysis of variability as a function of concentration, showing the relative precision at several percentiles in 6 concentration ranges or "bins," each of which contained from 16 to 52 observations. In part, the "jaggedness" of the lines results from the limited sample size in each bin, and also the varying MDLs for the different VOCs aggregated in each bin. Still, the figure shows general trends that aid the interpretation of measurement precision. No previous study is known to have reported this type of information.

While the median precision among replicates in the commuter study for concentrations from 0.5 to 1 µg m^{-3} is quite acceptable (analytical precision of 33%), some measurements are highly variable, *e.g.*, the 90th percentile analytical precision is 88%, meaning that 90% of replicates were within 88%. For VOCs concentrations from 1 to 3 µg m^{-3}, the median precision improves to 26%, but the 90th percentile precision decreases only slightly (87%). The variability decreases significantly, however, at concentrations above 10 µg m^{-3}.

In comparison to laboratory studies, field work involves many additional sources of variability and uncertainty that can affect replicate precision. In addition to recovery and analytical variability, the large sample volumes, higher humidity, and humidity variation may cause breakthrough and water management problems. In some cases, sample volumes of replicates differed considerably. Water management issues were noted by shifting of elution times in a number of samples. Other errors may arise due to inaccurate flow measurements and contamination of sorbent tubes during handling and transport. In comparison to the laboratory and IAQ (indoor air quality; described next) studies, the study involved many personnel, most of whom had had minimal training, and at times conditions were somewhat difficult due to scheduling and physical constraints.

Indoor air study. Table 7 shows the variety of aromatic, halogenated and terpene compounds found in the IAQ study.

Table 7 Results for indoor air quality study, based on 15 pairs of replicates (30 tubes in total)

	Concentration/$\mu g\ m^{-3}$			Precision (%)	Percent within precision limit[a]	
	Mean	Min	Max	Mean	$> \leqslant 20$	$\leqslant 50$
1,1,1-Trichloroethane	0.39	0.29	0.48	31	33	100
Benzene	1.04	0.45	2.53	14	60	100
Carbontetrachloride	0.15	0.05	0.28	38	27	73
Trichloroethylene	0.09	0.05	0.11	49	0	50
Toluene	5.20	0.50	29.36	17	73	93
Tetrachloroethylene	0.26	0.03	0.73	42	25	25
Ethylbenzene	0.51	0.08	1.40	15	73	100
p-Xylene, *m*-xylene	1.23	0.06	4.56	23	67	87
Styrene	0.10	0.04	0.22	24	44	100
o-Xylene	0.41	0.05	0.99	16	55	100
a-Pinene	0.36	0.33	0.41	2	100	100
1,3,5-Trimethylbenzene	0.10	0.02	0.26	38	25	75
Phenol	0.20	0.12	0.28	81	0	0
1,2,4-Trimethylbenzene	0.43	0.07	1.10	20	60	93
1,3-Dichlorobenzene	0.59	0.34	0.79	21	50	100
Limonene	5.18	1.33	28.84	10	85	100
Naphthalene	0.16	0.07	0.26	41	0	67
Mean				28	46	80

[a] The percentage for analytical precision within certain limit (*e.g.*, 20% or 50%).

Most VOCs were measured at low levels ($< 3\ \mu g\ m^{-3}$), with the exception of toluene, the xylenes, and limonene, which are associated with paints, fragrances, cleaning products and air fresheners. The other likely source of VOCs in this relatively clean building is infiltration of outside air that contains vehicular-related emissions. Indeed, simultaneous outside air measurements (not reported) showed that levels of fuel-related aromatics were very similar to indoor levels.

Analytical precisions in the IAQ study (Fig. 3) were better than those achieved in the ambient air study, *i.e.*, nearly all analytical precision value were within 50%. For concentrations $> 0.3\ \mu g\ m^{-3}$, the median precision was 20% and the 90th percentile precision was 38%. Several factors account for the higher performance. Samples were collected in moderate to low humidity (15–40% RH based on measurements at each sampling site), sample volumes tended to be smaller and more similar (typically 3.5–4.0 l), field personnel were highly trained, and transit times were shorter (1 h).

Comparison of laboratory and field studies

Overall, the laboratory studies of the 77 VOCs showed that method performance, in terms of tube cleanliness, reproducibility, sensitivity, selectivity, linearity, desorption efficiency and storage stability, met or far exceeded criteria required for trace level (ppb) measurements in ambient and indoor air. The method is particularly suitable for aromatic and halogenated compounds. Due to sorbent, column and MS detector characteristics, the performance was somewhat poorer for certain oxygen and nitrogen containing compounds.

Results in the two field studies generally supported the laboratory findings. Field study results must be interpreted carefully since they may involve multiple and often unknown sources of error. In the indoor air study, reproducibilities were as high as those achieved in the laboratory. In the ambient air study, reproducibilities among most replicate samples were within 40%, but considerably higher variation was observed for some compounds, *e.g.*, isopropylbenzene, 1,3-dichlorobenzene, *p*-isopropyltoluene and *n*-butylbenzene. This is believed to result from low concentrations and relatively high amounts of trapped water. The ambient study included a number of tubes that collected large volumes (> 5 l) of high humidity air samples. In contrast, sample volumes were smaller (and better controlled) in the indoor study, and the relative humidity was lower. The field studies show that sample volumes should not exceed 3 or perhaps 4 l unless additional water management steps are taken, or if the relative humidity during sampling is low.

Method modifications and improvements

This paper has evaluated a general method that can be used to analyze a wide range of non-polar and many polar VOCs present in air at low concentrations. Air sampling and analysis methods, like any other method, generally require a degree of optimization in order to meet special needs. Under humid environments, use of hydrophobic adsorbents, a more polar GC column, and a longer dry purge before analysis are suggested. Greater sensitivity to some compounds (and potentially greater dynamic range) can be achieved using electron capture, flame ionization detectors, or other detectors. It should be noted that the capabilities of the new desorber system and the current generation of GC-MS instruments have not been fully exploited, for example, pulsed split injection mode might be used to increase sample volumes.

System reliability. Several minor hardware problems were noted during the performance evaluation. These problems resulted from defective or binding screw threads on the sorbent tubes, connectors, needles and caps. Loose connectors result in leaks that may cause several types of problems. In the desorption process, leaks are detected by a large pressure drop when the needle pierces the GC septum, and the system will automatically halt prior to heating the sorbent tube, thus preserving sample integrity. The sorbent tube can be analyzed after correcting the leak. In storage, tubes that are not well sealed (due to binding threads, misfit or fallen-out Teflon washers) are prone to contamination.

Several steps were taken to rectify these problems, which occurred on a subset (17%) of the tubes. (Most of these tubes were preproduction samples obtained from the manufacturer.) First, we discarded bad tubes, caps, and needles. Second, the manufacturer has improved the machining of the threads, and newer components have been largely trouble-free. Third, we have suggested that the Teflon washers be slightly increased in diameter so that they are retained in the caps. Finally, treating the threads with Neolube® (Scientific Instrument Services) (fine graphite particles suspended in propan-2-ol) reduces binding and thus facilitates sealing. This treatment, which should be done on empty tubes to avoid contamination of the

sorbent, is simple: one drop of Neolube® is placed on the male threads, the tube is baked at 325 °C for 4 h, and the tube is packed with the sorbent as described previously. These steps have successfully eliminated binding problems.

Study limitations

Ideally, performance evaluations would take place under a large range of environmental conditions, and comparisons to a "reference" method would be used so that accuracy as well as precision could be established. In this study, the laboratory measurements were used to establish both accuracy and precision, and the field studies were used to evaluate analytical precision under fairly typical environmental conditions. Laboratory and field results appear consistent, however.

This study did not address all issues that might arise in air sampling. For example, sample collection and storage at very high or low temperatures were not evaluated. Sorbent break-through volumes and the use of alternate sorbents were not addressed. Only a subset of possible VOCs were studied. The availability of certified VOC standards at ppb levels would have facilitated analysis, and also enabled evaluation of very volatile compounds. It would be particularly interesting to study the performance of a short-path system for labile, reactive and/or extremely polar compounds that would be expected to be problematic for conventional methods. Many of these issues have been addressed elsewhere.[3,17,21] This analysis focused on the method and instrument.

Conclusion

Extensive laboratory and field tests have been used to evaluate the performance of an air sampling method involving active sampling onto Tenax GR and Carbosieve SIII sorbents; thermal desorption using a automated short-path system; and identification and quantification of VOCs using GC-MS. Results showed that tube cleanliness (blank emission <1 ng per sorbent tube), sensitivity (LOD $\leqslant 0.2$ ppb), reproducibility (RSDs $\leqslant 20\%$), linearity (%RSD of RRF $< 30\%$), desorption efficiency ($99\% \pm 30\%$), storage stability (low blanks, and RSDs $\leqslant 20\%$) and humid sample stability (recovery rates of $104\% \pm 11\%$ and $100\% \pm 13\%$ for 49% and 88% RH, respectively) meet or considerably exceed method requirements for ambient air and many other applications. In general, these results apply for a large range of target compounds. No carry-over (memory) problems were identified, as expected given the short-path configuration of the desorber system. The method is highly automated and reasonable throughput volumes can be achieved.

The performance evaluation is based on an examination of 77 common VOCs. While generally applicable to other compounds, some compounds (phenol groups, ketones, and nitrogen-containing VOCs) show lower reproducibilities and higher MDLs, largely due to the lower sensitivity of MS detector for these compounds and the use of a non-polar GC column. High sample volumes of humid air caused shifts in elution times that can degrade identification and quantification of non-specific detectors. These are generic issues in sorbent based air sampling that can be avoided or minimized by appropriate choices of sorbents, sample volumes and water management techniques, chromatography and detection methods.

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